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INTERNATION

INTERNATIONALE ZUSAMMENARBEIT AUF DEM GEBIET DES PATENTWESENS (PCT)

(51) Internationale Patentklassifikation ⁵ : A01N 25/22, 25/04 // (A01N 25/22 A01N 39/02, 43/00, 43/653 A01N 43/76, 43/78)	A1	(11) Internationale Veröffentlichungsnummer: WO 91/06215 (43) Internationales Veröffentlichungsdatum: 16. Mai 1991 (16.05.91)
(21) Internationales Aktenzeichen: PCT/EP90/01799 (22) Internationales Anmeldedatum: 24. Oktober 1990 (24.10.90) (30) Prioritätsdaten: P 39 35 977.8 28. Oktober 1989 (28.10.89) DE (71) Anmelder (für alle Bestimmungsstaaten ausser US): HOECHST AKTIENGESSELLSCHAFT [DE/DE]; Postfach 80 03 20, D-6230 Frankfurt am Main 80 (DE). (72) Erfinder; und (75) Erfinder/Anmelder (nur für US) : HEINRICH, Rudolf [DE/DE]; Taunusstraße 19, D-6233 Kelkheim (DE). MAIER, Thomas [DE/DE]; Rauenthaler Weg 22, D-6000 Frankfurt am Main (DE). SCHUMACHER, Hans [DE/DE]; Claudiusstraße 4, D-6093 Flörsheim am Main (DE).		(74) Gemeinsamer Vertreter: HOECHST AKTIENGESSELLSCHAFT; Zentrale Patentabteilung, Postfach 80 03 20, D-6230 Frankfurt am Main 80 (DE). (81) Bestimmungsstaaten: AT (europäisches Patent), AU, BE (europäisches Patent), CA, CH (europäisches Patent), DE (europäisches Patent), DK (europäisches Patent), ES (europäisches Patent), FR (europäisches Patent), GB (europäisches Patent), GR (europäisches Patent), HU, IT (europäisches Patent), JP, LU (europäisches Patent), NL (europäisches Patent), SE (europäisches Patent), SU, US. Veröffentlicht <i>Mit internationalem Recherchenbericht.</i>
(54) Title: SELECTIVE HERBICIDES (54) Bezeichnung: SELEKTIVE HERBIZIDE MITTEL (57) Abstract <p>The herbicides disclosed are stable compositions in the form of emulsion concentrates and containing: a) one or more herbicidal phenoxyphenoxy or heteroaryloxy-phenoxy carboxylic acid esters, b) one or more optionally substituted 1-aryl-3-alkoxydcarbonyl-5-alkyl-1,2,4-triazoles, c) one or more carboxylic or phosphoric acid esters of aliphatic mono-, di- or polyalcohols as stabilizing agents, d) one or more organic solvents, in particular a preponderance of aromatic solvents, e) one or more emulsifying agents and, optionally, wetting agents and other usually used additives.</p> (57) Zusammenfassung <p>Die erfindungsgemäßen Mittel sind stabile Formulierungen auf Basis von Emulsionskonzentraten und enthalten: a) einen oder mehrere herbizide Phenoxyphenoxy- oder Heteroaryloxy-phenoxy-carbonsäureester, b) ein oder mehrere Verbindungen aus der Gruppe der gegebenenfalls substituierten 1-Aryl-3-alkoxycarbonyl-5-alkyl-1,2,4-triazole, c) ein oder mehrere Carbonsäure- oder Phosphorsäureester von aliphatischen Mono-, Di- oder Polyalkoholen als stabilisierendes Agens, d) ein oder mehrere organische Lösungsmittel, insbesondere mit einem überwiegenden Teil an aromatischen Lösungsmitteln, und e) ein oder mehrere Emulgatoren und gegebenenfalls Netzmittel und übliche Zusatzstoffe.</p>		

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Description

Selective herbicidal agents

5 The invention relates to novel liquid selective herbicidal agents which contain active compounds from the group comprising phenoxy herbicides and optionally substituted 1-aryl-3-alkoxycarbonyl-5-alkyl-1,2,4-triazoles in the form of emulsion concentrates which are stable chemically and during use.

10 It is known that compounds from the group comprising phenoxy-phenoxy herbicides and benzoxazolyloxy-phenoxy herbicides can be combined with other compounds having a selective herbicidal action or with agents which protect crop plants (safeners) for the purpose of optimizing the
15 action spectrum to give finished formulations which are stable chemically and during use.

It is known, inter alia, from European Patent A-0,174,562 (US Patent A-4,639,266) that benzoxazolyloxy-phenoxy herbicides, such as, for example, ethyl 2-(4-(6-chloro-
20 2-benzoxazolyloxy)-phenoxy)-propionate ~~(-sio-)~~ (fenoxapropethyl) can be combined with safeners from the group comprising optionally substituted 1-aryl-3-alkoxycarbonyl-5-alkyl-1,2,4-triazole compounds by adding corresponding amounts of a formulation of the 1,2,4-
25 triazole mentioned to the spray liquor shortly before application of the fenoxapropethyl, so that the advantageous biological properties of the combination of the two active compounds can be utilized in this manner. However, this process is cumbersome and time-consuming, and can
30 easily lead to incorrect dosages in practice.

There was thus the object of avoiding these difficulties and of preparing biologically active homogeneous formulations of these two active compounds which are stable chemically and during use and which meet the requirements

imposed in practice.

5 It was to be remembered in particular that the two
classes of active compound can have an adverse influence
on each other in the presence of customary formulation
auxiliaries and stabilizers at elevated storage tempera-
tures and then undergo noticeable chemical changes,
especially over prolonged storage times, and lead to
components which are biologically less active or even
inactive. These disadvantages are overcome by the present
10 invention.

The present invention relates to liquid selective
herbicidal agents based on emulsion concentrates, which
contain

- 15 a) one or more herbicidal phenoxyphenoxy- or heteroaryl-
oxy-phenoxy-carboxylic acid esters,
- b) one or more compounds from the group comprising
optionally substituted 1-aryl-3-alkoxycarbonyl-5-
alkyl-1,2,4-triazoles,
- 20 c) one or more carboxylic acid esters or phosphoric acid
esters of aliphatic mono- di- or polyalcohols as a
stabilizing agent,
- d) one or more organic solvents, in particular with a
predominant content of aromatic solvents, and
- 25 e) one or more emulsifiers and if appropriate wetting
agents and customary additives.

30 The herbicidal phenoxy- or heteroaryloxy-phenoxy-
carboxylic acid esters which can be employed (component
a) are, for example, the known optionally substituted
phenoxyphenoxy-, quinoxalyloxyphenoxy-, pyridyloxy-
phenoxy-, benzoxazolyloxyphenoxy- or benzothiazolyloxy-
phenoxy-carboxylic acid esters, in the form of the pure

optical isomers or as isomer mixtures (for example racemates). The compounds are described, for example, in DE-A 2,136,828 (US-A 4,238,626); DE-A 2,223,894 (US-A 3,954,442); British Patent 2,0432,539 (sic); British
5 Patent 1,599,121; and DE-A 2,640,730 (US-A 4,130,413). The (C₁-C₄)alkyl, (C₂-C₄)alkenyl or (C₃-C₄)alkynyl esters are particularly suitable.

Suitable herbicides of component a) are, for example, the active compounds

10 methyl 2-(4-(2,4-dichlorophenoxy)-phenoxy)-propionate (diclofop-methyl),

methyl 2-(4-(4-bromo-2-chlorophenoxy)-phenoxy)-propionate,

15 methyl 2-(4-(4-trifluoromethylphenoxy)-phenoxy)-propionate,

methyl 2-(4-(2-chloro-4-trifluoromethylphenoxy)-phenoxy)-propionate,

ethyl 4-(4-(4-trifluoromethylphenoxy)-phenoxy)-pent-2-enoate,

20 ethyl 2-(4-(3,5-dichloropyridyl-2-oxy)-phenoxy)-propionate,

methyl or 2-ethoxyethyl 2-(4-(3-chloro-5-trifluoromethylpyridyl-2-oxy)-phenoxy)propionate (haloxyfop-methyl or haloxyfop-2-ethoxy-ethyl),

25 propargyl 2-(4-(3,5-dichloropyridyl-2-oxy)-phenoxy)-propionate,

ethyl 2-(4-(6-chlorobenzoxazol-2-yl-oxy)-phenoxy)-propionate (fenoxaprop-ethyl),

ethyl 2-(4-(6-chlorobenzothiazol-2-yl-oxy)-phenoxy)-
propionate (fenthiafop-ethyl),

methyl 2-(4-(3-chloro-5-trifluoromethyl-2-pyridyloxy)-
phenoxy)-propionate,

5 butyl 2-(4-(5-trifluoromethyl-2-pyridyloxy)-phenoxy)-
propionate ~~(sic)~~ (fluazifop-butyl),

ethyl 2-(4-(6-chloro-2-quinoxalyloxy)-phenoxy)-propionate
~~(sic)~~ (quizalofop-ethyl) and

10 ethyl 2-(4-(6-fluoro-2-quinoxalyloxy)-phenoxy)-
propionate.

The active compounds mentioned in the D,L- or in particu-
lar the enriched or pure D-form are preferred.

15 Agents according to the invention containing the herbi-
cidal active compound diclofop-methyl or fenoxaprop-ethyl
are particularly preferred. Most of the abovementioned
active compounds are also described in "The Pesticide
Manual", 8th edition 1987, British Crop. Protection
Council.

20 Suitable compounds for component b) of the agents accord-
ing to the invention are the compounds mentioned in
European Patent A-0,174,562, preferably the 1-(2,4-
dichlorophenyl)-3-(C₁-C₄-alkoxy)carbonyl-5-halogenoalkyl-
1,2,4-triazole compounds, in particular the 1-(2,4-
25 dichlorophenyl)-3-ethoxycarbonyl-5-halogenoalkyl-1,2,4-
triazoles, in which the halogenoalkyl radical is prefer-
ably CCl₃, CHCl₂ or CHF₂CF₂.

30 Low molecular weight esters of carboxylic acids or
phosphoric acids with alcohols, diols or polyols, for
example esters of aliphatic C₂-C₅-carboxylic acids or
phosphoric acid and linear or branched aliphatic C₂-C₁₂-
alcohols, -diols or -polyols, are of particular interest

as component c) having a stabilizing action. Preferred compounds here are esters of carboxylic acids, such as acetic acid, propionic acid, butanoic acid or pentanoic acid, in particular acetic acid, or of orthophosphoric acid with alcohols, such as methanol, ethanol, propanol, isopropanol, n-, i-, t- and 2-butanol, n-, i- or 2-pentanol, n-, i- or 2-hexanol, heptanol, octanol, nonanol, decanol, undecanol and dodecanol, or diols, such as glycol, propanediol, butanediol and hexanediol, or polyols, such as glycerol, pentaerythritol and hexitol.

Particularly preferred compounds are phosphoric acid esters, such as tri-n-butyl phosphate, or esters of acetic acid with C₂-C₈-alcohols or with diols, such as 1,4-butanediol, or with triols, such as glycerol, in particular the esters butyl acetate, pentyl acetate, hexyl acetate, heptyl acetate, nonyl acetate, 1,4-bis-(acetoxy)-butane and glycerol triacetate.

Organic solvents, such as aliphatic or aromatic hydrocarbons, aliphatic cyclic and acyclic ketones, N-methylpyrrolidone, dimethylformamide and alkylene glycol mono- and diesters or corresponding ethers, especially solvents having a high content of aromatics, are suitable, for example, as component d).

Examples of suitable aromatic solvents are toluene, xylenes, higher-boiling aromatic fractions and methylnaphthalenes, and a particularly suitable ketone is cyclohexanone.

Customary emulsifiers, preferably one or more from the group comprising alkylbenzenesulfonates, such as calcium dodecylsulfonate, and fatty acid polyglycol esters, such as ethoxylated castor oil, are suitable as component e). Any wetting agents contain d in the agents are preferably those from the group comprising alkylphenol polyglycol ethers and alkanol polyglycol ethers.

The ethoxylated castor oil or ethoxylated ricinic acid which can be employed according to the invention contains, in particular, 20 to 60 EO units (EO = ethylenoxy units). The products °Emulsogen EL 400 or °Emulsogen EL 360 (Hoechst AG), for example, can be employed. The fatty acid polyglycol esters contain, in particular, 12-18 carbon atoms in the fatty acid part. The ethoxylated alkylphenols are, in particular, nonylphenols and preferably contain 20-200 EO. These include, for example, °Arkopal N 100 (Hoechst AG). Ethoxylated (C₈-C₂₀)alkanols having an EO content of 3 to 20 EO, for example °Genapol X 060 (Hoechst AG) may be mentioned as preferred alkanol polyglycol ethers. Of the emulsifiers and wetting agents mentioned, ethoxylated castor oil and the alkanol polyglycol ethers are particularly suitable according to the invention.

The herbicidal agents according to the invention can contain further customary additives for emulsion concentrates, for example stabilizers against moisture, such as, for example, acid anhydrides, substituted amines and epoxide compounds, such as epoxidized linseed oil or soya oil.

The herbicidal agents according to the invention as a rule contain 5-50% by weight, preferably 20-35% by weight, of components a) and b), 2-20% by weight, in particular 5-15% by weight, of component c) and furthermore 5-40% by weight, preferably 10-25% by weight, of solvent and 10-30% by weight, preferably 15-25% by weight, of emulsifiers and wetting agents.

The ratio of the active compound components a) and b) to one another in the formulations is preferably 5:1 to 1:3. The optimum amount of component c) depends on the amount of active compounds a) and b) and can easily be determined in preliminary experiments.

The invention furthermore relates to a process for the

preparation of the agents according to the invention. For this, the abovementioned components are mixed with one another in the required amounts at temperatures of preferably 10° to 60°C, advantageously at room temperature or slightly above, until a homogeneous solution of the individual components has formed.

For carrying out the process in practice, the solvent or solvent mixture is first initially introduced into a tank with a stirrer; the two active compound components a) and b) are then added and the mixture is stirred until a clear solution is obtained. The compounds of component c) to be employed according to the invention are allowed to run slowly into this solution and the emulsifiers and if appropriate wetting agents and further additives are then added. The mixture is subsequently stirred until a clear solution is formed. The entire operation is advantageously carried out at room temperature or slightly above. The sequence of addition of the components can also be different.

The emulsion concentrate prepared, which corresponds to a practically anhydrous solution of components a), b), c) and e) in the organic solvent, is outstandingly stable towards chemical degradation of the active compounds and towards phase separations, such as, for example, the precipitation of components, even at comparatively high active compound contents. They therefore have a very good storage stability and are suitable for storage under climatically adverse conditions, in particular also at high temperatures of 30 to 50°C.

Before biological use of the emulsion concentrates, these are mixed with water to give emulsions which present no problems when used and which are not inferior in their activity to the combinations of the active compounds a) and b), formulated if appropriate, prepared in the spray tank.

The following Examples are intended to illustrate the invention in more detail:

Example 1

5 9.5% by weight of fenoxaprop-P-ethyl (I) (D-isomer of fenoxaprop-ethyl) are dissolved in 42% by weight of xylene at 25-30°C, while stirring. 4.7% by weight of 1-(2,4-dichlorophenyl)-3-ethoxycarbonyl-5-trichloromethyl-1,2,4-triazole (II) and then 12% by weight of a C₁₂-C₁₈-fatty alcohol polyglycol ether (containing 6 EO) and 6.8%
10 by weight of a C₁₂-C₁₈-fatty acid polyglycol ester (containing 40 EO) are added to the clear solution and the mixture is stirred until a clear solution is obtained.

15 5.0% by weight of epoxidized soya oil, 10.0% by weight of a xylene solution of the Ca salt of dodecylbenzenesulfonic acid and 10% by weight of glycerol triacetate are added to this solution and the mixture is subsequently stirred for 20 minutes.

A portion of the sample is stored at 50°C for 3 months and then analyzed:

20	Content,	Content after
	starting value	3 months/50°C
	Compound I 9.2% by weight	9.1% by weight
	Compound II 4.6% by weight	4.6% by weight

Comparison Example 1

25 The experiment from Example 1 is repeated, the same amount of xylene being added instead of 10% by weight of glycerol triacetate. The sample is likewise stored at 50°C for 3 months and then analyzed.

	Content, starting value	Content after 3 months/50°C
Compound I	9.2% by weight	8.6% by weight
Compound II	4.6% by weight	3.3% by weight

5 **Example 2**

12.5% by weight of fenoxaprop-P-ethyl (I) (= D-isomer of
fenoxaprop-ethyl) are dissolved in 35% by weight of
xylene at 25-30°C, while stirring. 8.8% by weight of 1-
10 (2,4-dichlorophenyl)-3-ethoxycarbonyl-5-trichloromethyl-
1,2,4-triazole (II) and then 10% by weight of a C₁₂-C₁₈-
fatty acid polyglycol ether (containing 8 EO) and 8.7% by
weight of a C₁₂-C₁₈-fatty acid polyglycol ester (containing
40 EO) are added to the clear solution and the mixture is
15 stirred until a clear solution is obtained. 5% by weight
of epoxidized linseed oil, 10.0% by weight of a xylene
solution of the Ca salt of dodecylbenzenesulfonic acid
and 10% by weight of tri-n-butyl phosphate are added to
this solution and the mixture is subsequently stirred for
about 20 minutes.

20 A portion of the sample is stored at 50°C for 3 months
and then analyzed:

	Content, starting value	Content after 3 months/50°C
Compound I	11.8% by weight	11.7% by weight
25 Compound II	8.2% by weight	8.2% by weight

Comparison Example 2

The experiment from Example 2 is repeated, but instead of
the 10% by weight of tri-n-butyl phosphate the same
amount of xylene is added. The sample is likewise stored
30 at 50°C for 3 months and then analyzed.

	Content, starting value	Content after 3 months/50°C
Compound I	11.6% by weight	9.9% by weight
Compound II	8.1% by weight	6.5% by weight

5 **Example 3**

16.5% by weight of fenthia-*prop*-ethyl (III) are dissolved in 42% by weight of xylene at 25-30°C, while stirring. 8.2% by weight of 1-(2,4-dichloro-phenyl)-3-ethoxycarbonyl-5-trichloromethyl-1,2,4-triazole (II) and then 5% by weight of a C₁₂-C₁₈-fatty alcohol polyglycol ether (containing 10 EO) and 6.3% by weight of a C₁₂-C₁₈-fatty acid polyglycol ester (containing 36 EO) are added to this clear solution and the mixture is stirred until a clear solution is obtained. 5% by weight of epoxidized linseed oil, 5% by weight of calcium dodecylbenzenesulfonate and 12% by weight of hexyl acetate are added to this solution and the mixture is subsequently stirred for about 20 minutes.

A portion of the sample is stored at 50°C for 3 months and then analyzed:

	Content, starting value	Content after 3 months/50°C
Compound III	15.6% by weight	15.4% by weight
Compound II	7.7% by weight	7.6% by weight

25 **Comparison Example 3**

The experiment from Example 3 is repeated, but instead of the 12% by weight of hexyl acetate the same amount of xylene is added. The sample is likewise stored at 50°C for 3 months and then analyzed.

	Content, starting value	Content after 3 months/50°C
Compound I	15.5% by weight	13.9% by weight
Compound II	7.6% by weight	6.0% by weight

5 **Example 4**

The procedure is analogous to Example 1, but 1-(2,4-dichlorophenyl)-3-ethoxycarbonyl-5-dichloromethyl-1,2,4-triazole is employed as the triazole compound. A comparably stable emulsion concentrate is obtained.

10 **Example 5**

The procedure is analogous to Example 2, but 1-(2,4-dichlorophenyl)-3-ethoxycarbonyl-5-(1,1,2,2-tetrafluoroethyl)-1,2,4-triazole is employed as the triazole compound. The resulting emulsion concentrate is stable at 15 50°C for 3 months and in particular exhibits no noticeable degradation of the active compound content.

Biological Examples

The emulsion concentrates obtained according to the preparation examples are diluted to the use concentration 20 with water and used against monocotyledon or dicotyledon or mono- and dicotyledon weeds in field experiments.

The biological studies show that there are no noticeable differences between the finished formulations and the combinations of the individual active compounds prepared 25 in the spray tank (tank mixture) either in plant tolerance or in herbicidal action.

Patent Claims:

1. A liquid herbicidal agent based on an emulsion concentrate, which contains

5 a) one or more herbicidal phenoxyphenoxy- or hetero-aryloxy-phenoxy-carboxylic acid esters,

b) one or more compounds from the group comprising optionally substituted 1-aryl-3-alkoxycarbonyl-5-alkyl-1,2,4-triazoles,

10 c) one or more carboxylic acid esters or phosphoric acid esters of aliphatic mono- di- or polyalcohols as a stabilizing agent,

d) one or more organic solvents,
and

15 e) one or more emulsifiers and if appropriate wetting agents and customary additives.

20 2. An agent as claimed in claim 1, which contains optionally substituted phenoxyphenoxy-, quinoxalyl-oxyphenoxy-, pyridyloxyphenoxy-, benzoxazolyloxyphenoxy- or benzothiazolyloxyphenoxy-carboxylic acid esters as component a).

3. An agent as claimed in either of claims 1 or 2, which contains 1-(2,4-dichlorophenyl)-3-(C₁-C₄-alkoxy)-carbonyl-5-halogenoalkyl-1,2,4-triazole compounds as component b).

25 4. An agent as claimed in any one of claims 1 to 3, which contains esters of C₂-C₅-carboxylic acids or phosphoric acid and linear or branched aliphatic C₂-C₁₂-alcohols, diols or polyols as component c).

5. An agent as claimed in any one of claims 1 to 4,

which contains toluene, xylenes, higher-boiling aromatic fractions, methylnaphthalenes or cyclohexanone as the solvent.

6. An agent as claimed in any one of claims 1 to 5, which contains customary emulsifiers and wetting agents from the group comprising alkylbenzenesulfonates, fatty acid polyglycol esters and alkylphenol ethers and alkanol polyglycol ethers as component (e).
7. An agent as claimed in any one of claims 1 to 6, which contains 5-50% by weight of components (a) and (b), 2-20% by weight of component (c), 5-40% by weight of solvent and 10-30% by weight of emulsifiers and wetting agents.
8. An agent as claimed in claim 7, which contains
20-35% by weight of components (a) and (b),
5-15% by weight of component (c);
10-25% by weight of solvent; and
15-25% by weight of emulsifiers and wetting agents.
9. An agent as claimed in any of claims 1 to 8 wherein the component (a) is ethyl (D,L)- or ethyl (D)-2-(4-(-6-chlorobenzoxazol-2-yloxy)-phenoxy)-propionate.
10. A process for the preparation of a herbicidal agent defined as claimed in any one of claims 1 to 9, which comprises mixing the components (a) to (e) at 10 to 60°C until a homogeneous solution of all the components has formed.

11. A method for preparing an aqueous herbicidal emulsion wherein an emulsion concentrate as claimed in any one of claims 1 to 9 is mixed with water.

DATED this 14th day of July, 1993

HOECHST AKTIENGESELLSCHAFT

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AUSTRALIA

Abstract of the disclosure:

Selective herbicidal agents

The agents according to the invention are stable formulations based on emulsion concentrates and contain

- a) one or more herbicidal phenoxyphenoxy- or heteroaryloxy-phenoxy-carboxylic acid esters,
- b) one or more compounds from the group comprising optionally substituted 1-aryl-3-alkoxycarbonyl-5-alkyl-1,2,4-triazoles,
- c) one or more carboxylic acid esters or phosphoric acid esters of aliphatic mono- di- or polyalcohols as a stabilizing agent,
- d) one or more organic solvents, in particular, with a predominant content of aromatic solvents, and
- e) one or more emulsifiers and if appropriate wetting agents and customary additives.

INTERNATIONAL SEARCH REPORT

International Application No PCT/EP90/01799

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) *		
According to International Patent Classification (IPC) or to both National Classification and IPC		
Int. Cl. ⁵ : A01N 25/22, 25/04// (A01N 25/22, 39:02, 43:00, 43:653, 43:76, 43:78)		
II. FIELDS SEARCHED		
Minimum Documentation Searched ?		
Classification System	Classification Symbols	
Int. Cl. ⁵	A01N	
Documentation Searched other than Minimum Documentation to the extent that such Documents are included in the Fields Searched *		
III. DOCUMENTS CONSIDERED TO BE RELEVANT *		
Category *	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
Y	EP, A2, 0174562 (HOECHST AG) 19 March 1986, see page 8, line 18-page 9, line 23; page 12, line 1-line 14; page 14, line 20-page 15, line 11; page 32-page 39, claims 1,4-7	1-10
Y	EP, A1; 0085922 (HOECHST AG) 17 August 1983, see claims	1-10
Y	EP, A1, 0102003 (S.I.P.C.A.M. S.P.A. SOCIETA ITALIANA PRODOTTI CHIMICI E PER L'AGRICOLTURA MILANO) 7 March 1984, see claims	1-10
Y	GB, A, 2176108 (RHONE-POULENC AGROCHIMIE) 17 December 1986, see claims 1,2	1-10
<p>* Special categories of cited documents: ¹⁰</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"&" document member of the same patent family</p>		
IV. CERTIFICATION		
Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report	
16 January 1991 (16.01.91)	6 February 1991 (06.02.91)	
International Searching Authority	Signature of Authorized Officer	
European Patent Office		

**ANNEX TO THE INTERNATIONAL SEARCH REPORT
ON INTERNATIONAL PATENT APPLICATION NO. PCT/EP 90/01799**

SA 41132

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on 28/11/90. The European Patent office is in no way liable for these particulars which are merely given for the purpose of information.

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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		NL-A- 8601397	02/01/87

For more details about this annex : see Official Journal of the European patent Office, No. 12/82

INTERNATIONALER RECHERCHENBERICHT

Internationales Aktenzeichen PCT/EP 90/01799

I. KLASSIFIKATION DES ANMELDUNGS ENSTANDS (bei mehreren Klassifikationssymbolen sind alle anzugeben) ⁶		
Nach der Internationalen Patentklassifikation (IPC) oder nach der nationalen Klassifikation und der IPC		
InLCI ⁵ A 01 N 25/22, 25/04/(A 01 N 25/22, 39:02, 43:00, 43:653 43:76, 43:78)		
II. RECHERCHIERTE SACHGEBIETE		
Recherchierter Mindestprüfstoff ⁷		
Klassifikationssystem	Klassifikationssymbole	
InLCI ⁵	A 01 N	
Recherchierte nicht zum Mindestprüfstoff gehörende Veröffentlichungen, soweit diese unter die recherchierten Sachgebiete fallen ⁸		
III. EINSCHLÄGIGE VERÖFFENTLICHUNGEN ⁹		
Art *	Kennzeichnung der Veröffentlichung ¹¹ , soweit erforderlich unter Angabe der maßgeblichen Teile ¹²	Betr. Anspruch Nr. ¹³
Y	EP, A2, 0174562 (HOECHST AG) 19 März 1986, siehe Seite 8, Zeile 18 - Seite 9, Zeile 23; Seite 12, Zeile 1 - Zeile 14; Seite 14, Zeile 20 - Seite 15, Zeile 11; Seite 32 - Seite 39, Ansprüche 1,4-7	1-10
Y	EP, A1, 0085922 (HOECHST AG) 17 August 1983, Siehe Ansprüche	1-10
Y	EP, A1, 0102003 (S.I.P.C.A.M. S.P.A. SOCIETA ITALIANA PRODOTTI CHIMICI E PER L'AGRICOLTURA MILANO) 7 März 1984, Siehe Ansprüche	1-10
<p>* Besondere Kategorien von angegebenen Veröffentlichungen¹⁰:</p> <p>"A" Veröffentlichung, die den allgemeinen Stand der Technik definiert, aber nicht als besonders bedeutsam anzusehen ist</p> <p>"E" älteres Dokument, das jedoch erst am oder nach dem internationalen Anmeldedatum veröffentlicht worden ist</p> <p>"L" Veröffentlichung, die geeignet ist, einen Prioritätsanspruch zweifelhaft erscheinen zu lassen, oder durch die das Veröffentlichungsdatum einer anderen im Recherchenbericht genannten Veröffentlichung belegt werden soll oder die aus einem anderen besonderen Grund angegeben ist (wie ausgeführt)</p> <p>"O" Veröffentlichung, die sich auf eine mündliche Offenbarung, eine Benutzung, eine Ausstellung oder andere Maßnahmen bezieht</p> <p>"P" Veröffentlichung, die vor dem internationalen Anmeldedatum, aber nach dem beanspruchten Prioritätsdatum veröffentlicht worden ist</p> <p>"T" Spätere Veröffentlichung, die nach dem internationalen Anmeldedatum oder dem Prioritätsdatum veröffentlicht worden ist und mit der Anmeldung nicht kollidiert, sondern nur zum Verständnis des der Erfindung zugrundeliegenden Prinzips oder der ihr zugrundeliegenden Theorie angegeben ist</p> <p>"X" Veröffentlichung von besonderer Bedeutung, die beanspruchte Erfindung kann nicht als neu oder auf erfinderischer Tätigkeit beruhend betrachtet werden</p> <p>"Y" Veröffentlichung von besonderer Bedeutung, die beanspruchte Erfindung kann nicht als auf erfinderischer Tätigkeit beruhend betrachtet werden, wenn die Veröffentlichung mit einer oder mehreren anderen Veröffentlichungen dieser Kategorie in Verbindung gebracht wird und diese Verbindung für einen Fachmann naheliegend ist</p> <p>"&" Veröffentlichung, die Mitglied derselben Patentfamilie ist</p>		
IV. BESCHEINIGUNG		
Datum des Abschlusses der internationalen Recherche	Absendedatum des internationalen Recherchenberichts	
16. Januar 1991	- 6 FEB 1991	
Internationale Recherchenbehörde	Unterschrift des bevollmächtigten Bediensteten	
Europäisches Patentamt	PROF. D. S. ...	

III. EINSCHLÄGIGE VERÖFFENTLICHUNGEN (Fortsetzung von Blatt 2)		
Art *	Kennzeichnung der Veröffentlichung, soweit erforderlich unter Angabe der wesentlichen Teile	Betr. Anspruch Nr.
Y	GB. A, 2176108 (RHONE-POULENC AGROCHIMIE) 17 Dezember 1986, siehe Ansprüche 1,2 -----	1-10

ANHANG ZUM INTERNATIONALEN RECHERCHENBERICHT ÜBER DIE INTERNATIONALE PATENTANMELDUNG NR.PCT/EP 90/01799

SA 41132

In diesem Anhang sind die Mitglieder der Patentfamilien der im obengenannten internationalen Recherchenbericht angeführten Patentdokumente angegeben.
Die Angaben über die Familienmitglieder entsprechen dem Stand der Datei des Europäischen Patentamts am 28/11/90
Diese Angaben dienen nur zur Unterrichtung und erfolgen ohne Gewähr.

Im Recherchenbericht angeführtes Patentdokument	Datum der Veröffentlichung	Mitglied(er) der Patentfamilie	Datum der Veröffentlichung
EP-A2- 0174562	19/03/86	AU-B- 581459	23/02/89
		AU-D- 4732285	20/03/86
		DE-A- 3525205	20/03/86
		JP-A- 61068474	08/04/86
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		DE-A- 3618535	12/02/87
		FR-A- 2590119	22/05/87
		NL-A- 8601397	02/01/87

Für nähere Einzelheiten zu diesem Anhang : siehe Amtsblatt des Europäischen Patentamts, Nr.12/82

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